CALCULATION OF TOTAL CROSS SECTIONS

FOR CHARGE EXCHANGE IN MOLECULAR COLLISIONS

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Juliette Ioup,Principal Investigator
Physics Department
Xavier University
New Orleans, La 70125

CALCULATIONS OF TOTAL CROSS SECTIONS FOR CHARGE EXCHANGE IN MOLECULAR COLLISIONS

INTRODUCTION

Research accomplished during the first six months of the grant may be divided into two main areas. The first concerned the theoretical investigation of low energy collisions of nitrogen ions with nitrogen molecules. Related experimental research was performed at Langley Research Center by Dr. Al Smith of the Instruments Research Division. The effort under this grant was to apply theories reported in the literature to this specific collision. The calculations and results are given in the attached reports on pages 2 through 20.

The second project was a preliminary search of the literature on collisions of low energy ions with surfaces for the purpose of extending the present research. The initial listing of some reference materials (books, articles, papers, etc.) is attached on page 21. In addition, a partial literature search was made through the recently acquired Xavier Information Program, a computer search of selected data banks. It is planned to use the NASA library search service and to repeat the Xavier search when access to more abstracts and data banks becomes available.

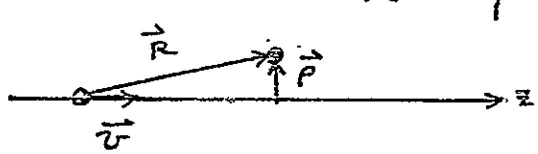
MULTISTATE IMPACT PARAMETER METHOD

This outline of the multistate impact parameter method for the theoretical treatment of molecular charge transfer follows closely that given by Flannery, Cosby, and Moran[1] and uses their notation. The method[2] attempts to take into account the vibrational states of the incident ions and of the products, with the target neutral molecules assumed to be initially in the ground state. Total cross sections for N_2^+ on N_2 are obtained.

The charge-transfer process in diatomic nitrogen is resonant and symmetric so that the wavefunction $\Psi(t)$ may be expanded in terms of the gerade and ungerade eigenfunctions $\chi_{g,u}(\vec{r},\vec{R})$ for each electronic state of the quasimolecular complex formed. The atomic separation in the molecule is $\vec{r}$ and the distance between the two centers of mass is $\vec{R}$. The relative phase η changes with R because of differences in the eigenenergies $\epsilon_{g,u}(R)$. Charge transfer does not occur because of an electronic transition but because of this phase change.[3]

Assume a straight line trajectory

$$\vec{R} = \vec{\rho} + \vec{v}t \qquad (1)$$



where ρ is the impact parameter and v is the incident speed along the z-axis. The probability for symmetrical resonant charge transfer is

$$P_M^X(\rho) = \sin^2 \eta(\rho) \qquad (2)$$

for a two-state gerade-ungerade treatment, where

$$\eta = \frac{1}{v} \int_0^\infty [\epsilon_g(R) - \epsilon_u(R)]\, dz \qquad (3)$$

The charge-transfer cross section is

$$\sigma = 2\pi \int_0^\infty \sin^2 \eta(\rho)\, \rho\, d\rho \qquad (4)$$

In order to include nonresonant channels, the wavefunction is expanded[2] in terms of $\phi_n^\alpha(\vec{r})$, the molecular eigenfunctions of the unperturbed Hamiltonian for the isolated molecular systems. The $\phi_n^\alpha(\vec{r})$ have electronic, vibrational, and rotational parts, and the eigenenergies at infinite center-of-mass separation are E_n^α.

$$\Psi(t) = \sum_{\alpha = D,X} \sum_n a_n^\alpha(t)\, \phi_n^\alpha(\vec{r})\, e^{-iE_n^\alpha t} \qquad (5)$$

The index α refers to either the direct channels D (no charge transfer) or to the exchange channels X. This expansion is substituted into the time-dependent Schrodinger equation for the internal coordinates. The charge-transfer cross section then derived[2] is

$$\sigma = 2\pi \int_0^\infty |C_f^X(\rho,\infty)|^2\, \rho\, d\rho \qquad (6)$$

to lowest order. The transition amplitudes $C_f^X(\rho, t)$ are the solutions to the set of first-order coupled differential equations

$$i \frac{\partial C_\ell^\alpha}{\partial t} = V(R) \sum_{m=1}^{N} P_{\ell m} C_m^{\bar{\alpha}}(\rho, t) e^{i(E_\ell - E_m)t} , \quad \ell = 1, 2, \ldots N \qquad (7)$$

where $\bar{\alpha} = X$ when $\alpha = D$ and vice versa. Only the direct channel i is occupied initially:

$$\begin{aligned} C_m^D(\rho, -\infty) &= \delta_{mi} \\ C_m^X(\rho, -\infty) &= 0 \end{aligned} \qquad (8)$$

The matrix elements $P_{\ell m}$ are

$$P_{\ell m} = F(\nu_\ell' \, \nu_m'') F(\nu_m' \, \nu_\ell'') \qquad (9)$$

where $F(\nu_i' \, \nu_n'')$ is the vibrational overlap of the incident ion in the ν_i' vibrational state and the target neutral in the ν_n'' vibrational state. The rotational motion is neglected since the energies are such that the collision is finished before the molecular complex can rotate significantly.[1] The interaction potential V(R) is assumed to be spherically symmetric and can be obtained from the gerade-ungerade splitting of the vibrational motion.[1]

$$V(R) = \frac{1}{2} \left[\epsilon_g(R) - \epsilon_u(R) \right] \qquad (10)$$

Then the exchange cross section becomes

$$\sigma = 2\pi \int_0^\infty \rho \sin^2 \left[\frac{2}{v} \int_0^\infty V(R) \, dz \right] \qquad (11)$$

The gerade potential is given by the Morse function[4]

$$\epsilon_g(R) = D_e\left[e^{-2\beta(R-R_e)} - 2e^{-\beta(R-R_e)}\right] \quad (12)$$

where R_e is the internuclear distance corresponding to the potential minimum of depth D_e, and β describes the shape of the potential. The modified Lennard-Jones potential[5,6]

$$V_{LJ4} = 4\epsilon\left[\left(\frac{d}{R}\right)^{12} - \left(\frac{d}{R}\right)^{6}\right] - \frac{\alpha e^2}{2R^4} \quad (13)$$

where α is the polarizability and ϵ and d are Lennard-Jones parameters which are known for the nitrogen potential,[7] gives the interaction energy for the gerade state for this reaction. Fitting the Morse curve to the Lennard-Jones potential allows determination of the parameters $R_e = 3.5262$ Å, $D_e = 0.06917$ eV, and $\beta = 1.5903$ Å^{-1} for nitrogen.[1]

Sato[8] proposed that the ungerade potential may be written as

$$\epsilon_u(R) = \frac{1}{2}D_e\left[e^{-2\beta(R-R_e)} + 2e^{-\beta(R-R_e)}\right] \quad (14)$$

The interaction potential $V(R)$ from Eq. (10) is therefore obtained to be

$$V(R) = \begin{cases} \frac{1}{4}D_e e^{-2\beta(R-R_e)} - \frac{3}{2}D_e e^{-\beta(R-R_e)} & R > R^* \\ 0 & R < R^* \end{cases} \quad (15)$$

$V(R)$ is set equal to zero for small $R < R^*$, where $R^* \equiv R_e - \ln 6/\beta = 2.3995$ Å for N_4^+, since negative values of the interaction potential are unphysical. Since D_e, R_e, and β have been determined, the interaction potential is now known.

Vibrational overlaps are needed in order to obtain the transition amplitudes C_f^X for the charge-transfer cross section in Eq. (6). Overlaps for diatomic ions and neutral molecules in the ground state are given by Nicholls.[9] Flannery et al[1] computed overlaps for excited states of the neutral using the Franck-Condon factors[9] with a Morse anharmonic oscillator wavefunction.[9,10] The excitation defects of various reaction channels were computed from spectroscopic energy levels[4,11,12] of the ionic and neutral species. They found[1] that the excitation defects occurred in groups or "bands" separated by approximately one vibrational quantum of energy, about 0.25 eV.[13] Therefore the channels could be considered to be degenerate within a given band, greatly simplifying the calculations involved. The transition probabilities $P_{\ell m} = \left|C_f^X\right|^2$ were obtained as a function of impact parameter ρ by solving the multistate Equations (7) numerically by the Adams-Moulton method.[14] The charge transfer cross sections σ were obtained from Eq. (6) using these transition probabilities by numerical integration over impact parameter

using Simpson's Rule with a built-in accuracy parameter.

The low-velocity approximation[2] can be used for collisions in which the incident velocity is small enough so that the excitation defect $E_\ell - E_m$ is approximately zero. Then Equations (7) for the transition probability become

$$i \frac{\partial C_\ell^\alpha}{\partial t} = V(R) \sum_{m=1}^{B} P_{\ell m} C_m^{\bar{\alpha}}(\rho, t) \qquad \ell = 1, 2, \cdots B \tag{16}$$

where B is the number of degenerate final states which have zero energy defect with the incident energies. The exchange cross section then becomes

$$\sigma = 2\pi \sum_{n=1}^{B} X_{in}^2 \int_0^\infty \rho \sin^2\left[\frac{\Pi_n}{v} \int_{-\infty}^{\infty} V(R)\, dz\right] d\rho \tag{17}$$

where the Π_n are the eigenvalues and the X_{in} the associated eigenfunctions of the matrix which diagonalizes the matrix P formed from the $P_{\ell m}$:

$$\Pi = X^{-1} P X = \tilde{X} P X \tag{18}$$

Some representative results of both the low-velocity approximation and the full multistate treatment as well as some additional experimental data from the literature are presented in the accompanying figures for comparison with the Langley data.

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FIGURE DISCUSSIONS

Figs. 1-3 present total charge-transfer cross sections for N_2^+ on N_2 obtained at different pressures in the charge transfer cell as a function of the square root of the incident ion kinetic energy. Each figure contains data points obtained at pressures in the CTC of 0.99, 1.33, 1.66, and 1.987 x 10^{-4} Torr. Fig. 1 shows cross sections obtained for ionizing electron energy of 16 eV, Fig. 2 for electron energy 17.5 eV, and Fig. 3 for electron energy 19.5 eV.

Figs. 4-7 show the same data of total charge-transfer cross sections for N_2^+ on N_2 as a function of the square root of incident ion kinetic energy. Each plot contains data for the three different ionizing electron energies (16.0, 17.5, and 19.5 eV) with a separate figure for each different pressure in the CTC.

Fig. 8 compares the Langley experimental results with similar data from the literature and with the theoretical calculations of Flannery et al.[1] Since most of the data for comparison were for ionizing electron energies much higher than the present values, the data obtained using the largest electron energy of 19.5 eV at an intermediate CTC pressure of 1.66 x 10^{-4} Torr was

chosen for comparison. It can be seen from the previous seven figures that the other cross section data falls in the same region. The Langley data is shown as filled circles in Fig. 8. The full multistate treatment (M) and the low-velocity approximation (LV) were calculated by Flannery et al[1] using the distribution of vibrational levels in the incident ion beam corresponding to an electron excitation energy of 22 eV. The experimental data obtained by this group is not included in Fig. 8 since results were published only for ion energies of 733 eV and higher. Ghosh and Sheridan[2] (GS) state that the N_2^+ ions are in the ground state when leaving their Heil type ion source. Pressure in their collision chamber was measured by a Knudsen gauge to be 1.7 x 10^{-4} Torr. Potter[3] (P) also claims to have only ground state $N_2^+(X^2\Sigma_g^+)$ ions in his incident beam, although Ghosh and Sheridan[2] disagree with his statement. The electron energy in the ion source of Stebbings, Turner, and Smith[4] (STS) was 200 eV. Utterback and Miller[5] (UM) used only 22 eV electrons in their ion source, and the pressure in their collision region was 2 x 10^{-4} Torr. Some data of Berry[6] (B) and Gustafson and Lindholm[7] (GL) are also presented in Fig. 8 for comparison. Nichols and Witteborn[8] (NW) measured total cross sections at very low ion energies of less than 17 eV. Electron energies in their ion source were 95 eV, and their reaction chamber pressure was between 8 x 10^{-4} and 10^{-6} Torr.

Moran et al[9] used the multistate impact parameter method[1] to obtain cross sections for individual channels and integral cross sections summed over all product channels. Theoretical cross sections were obtained as a function of the square root of incident ion kinetic energy for nitrogen when both the incident ion and target neutral were in the ground electronic and vibrational state and the resultant product neutral υ and ion υ' in vibrational states (υ, υ') equal to (0,1), (1,0), and (0,2), and for total vibrational excitation of the products. These cross sections presented in Fig. 9 of Ref. 9 were less than 4 Å^2 for all cases, decreasing to less than 1 Å^2 for incident ion energies of about 900 eV. They also obtained theoretical cross sections for total vibrational excitation with the incident ion in the ground electronic state $N_2^+(X^2\Sigma_g^+)$ and vibrational states 0,1,2,3 with the target neutral in the ground electronic and vibrational state $N_2(X^1\Sigma_g^+, \upsilon=0)$ as a function of incident ion kinetic energy. These cross sections presented in Fig. 10 of Ref. 9 were less than 10 Å^2 for incident energies larger than about 25 eV. Since the cross sections were so much smaller than the other data, they were not included in Fig. 8.

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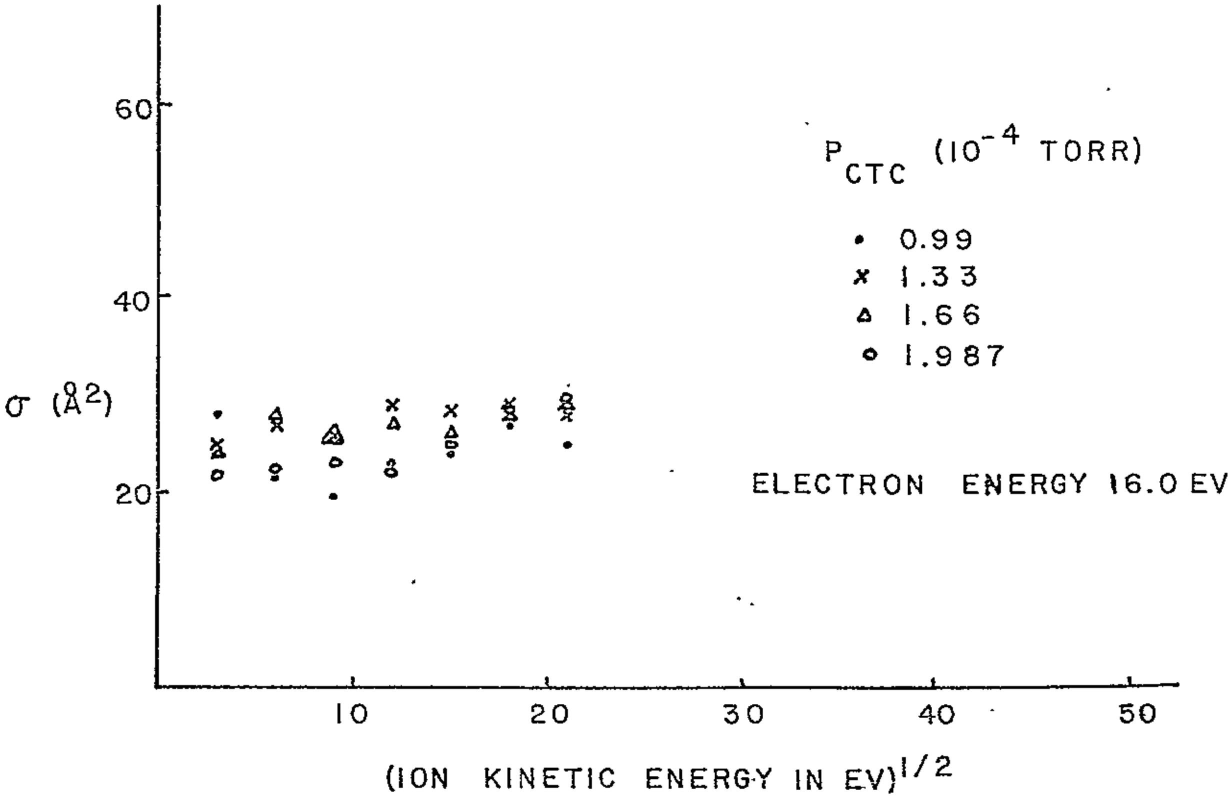
60
40
20
σ (Å²)
P_{CTC} (10^{-4} TORR)
• 0.99
× 1.33
△ 1.66
○ 1.987
ELECTRON ENERGY 16.0 EV
10
20
30
40
50
(ION KINETIC ENERGY IN EV)$^{1/2}$

Fig. 1

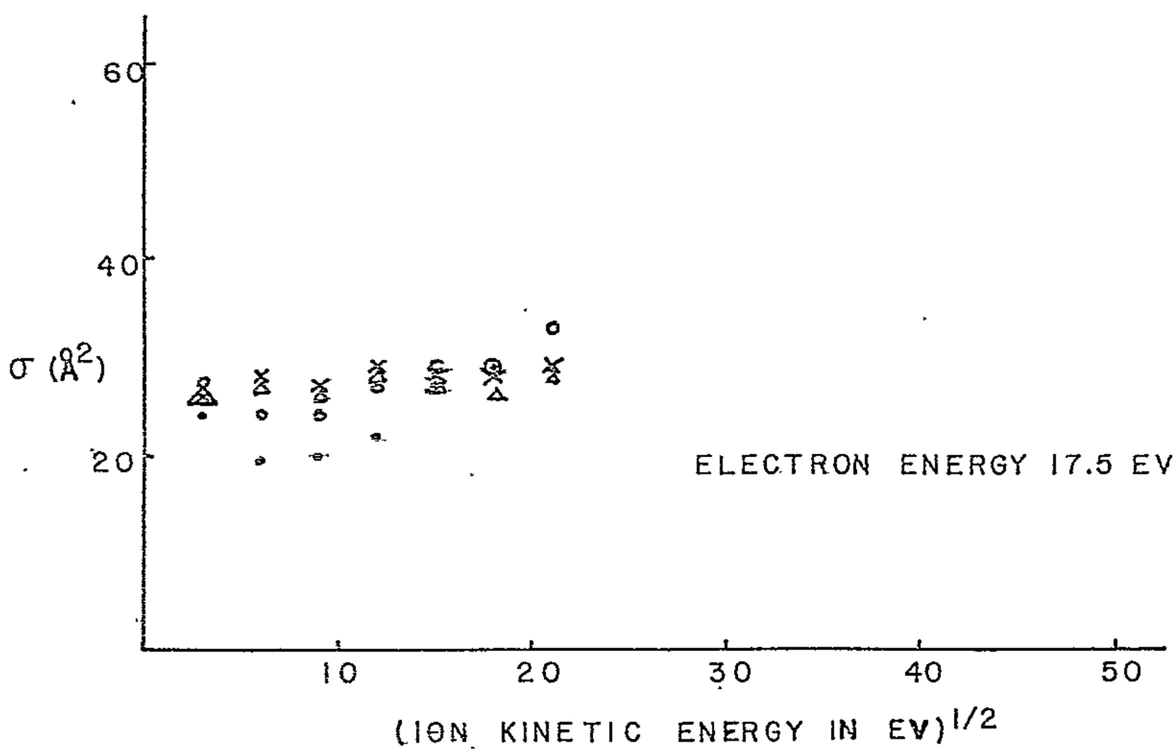
60
40
20
σ (Å²)
ELECTRON ENERGY 17.5 EV
10
20
30
40
50
(ION KINETIC ENERGY IN EV)$^{1/2}$

Fig. 2

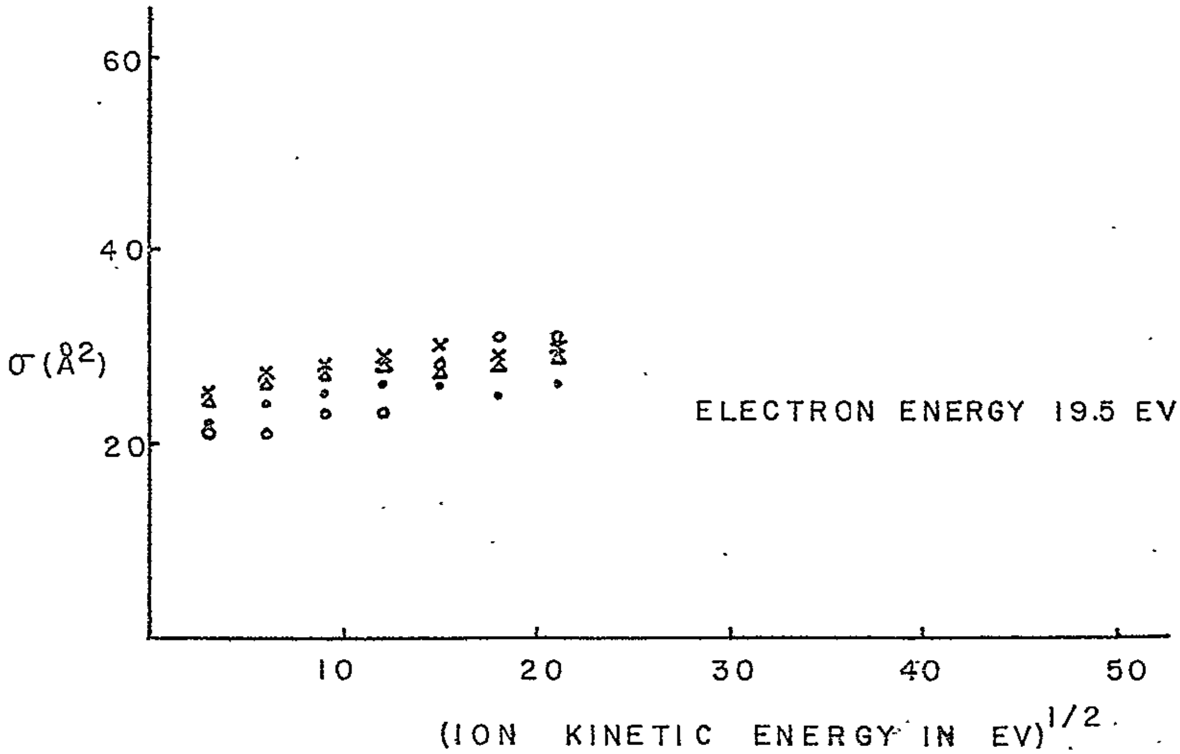
60
40
20
σ (Å²)
ELECTRON ENERGY 19.5 EV
10
20
30
40
50
(ION KINETIC ENERGY IN EV)1/2

Fig. 3

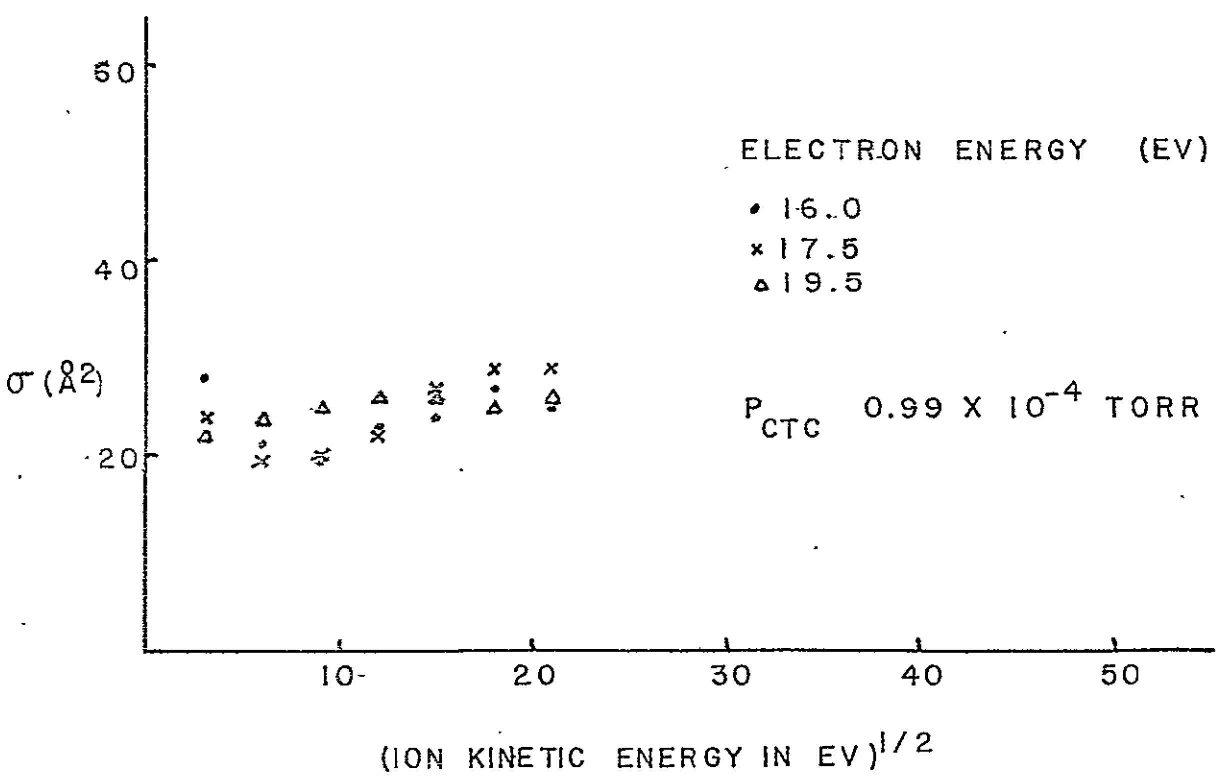
50
40
20
σ (Å²)
ELECTRON ENERGY (EV)
• 16.0
× 17.5
△ 19.5
P CTC 0.99 X 10-4 TORR
10
20
30
40
50
(ION KINETIC ENERGY IN EV)1/2

Fig. 4

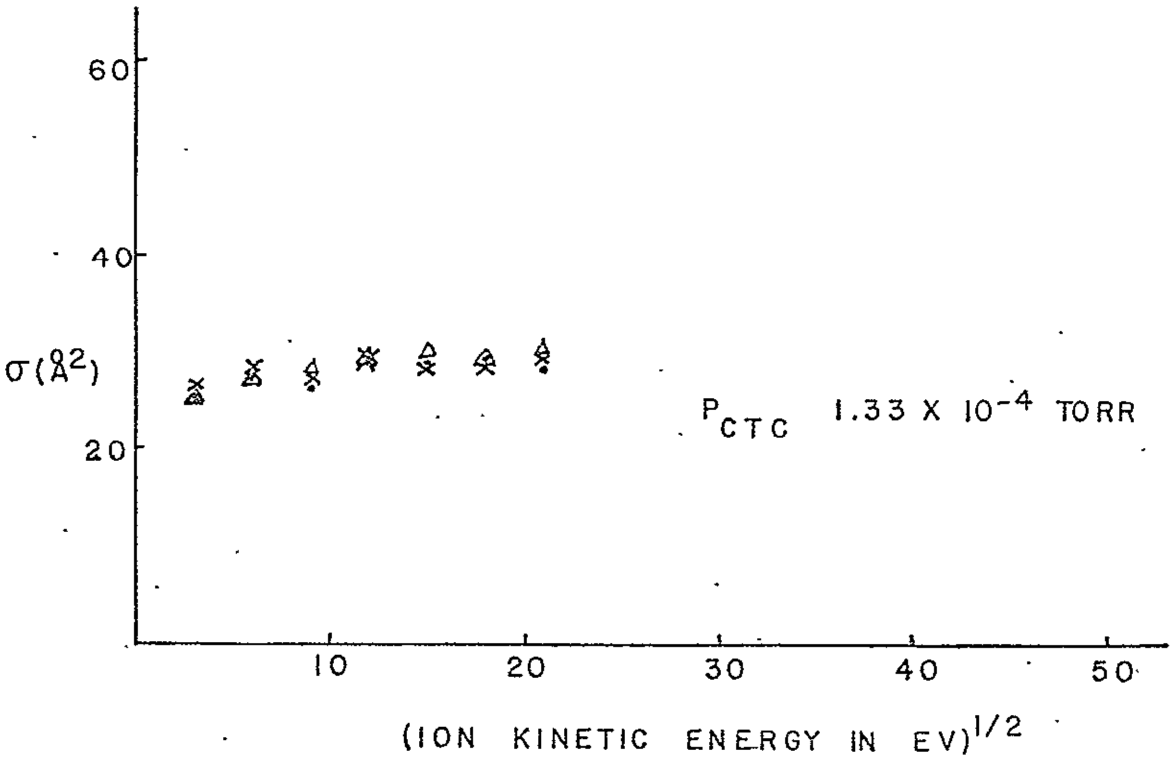
60
40
20
σ(Å²)
10
20
30
40
50
(ION KINETIC ENERGY IN EV)^1/2
P CTC 1.33 X 10^-4 TORR

Fig. 5

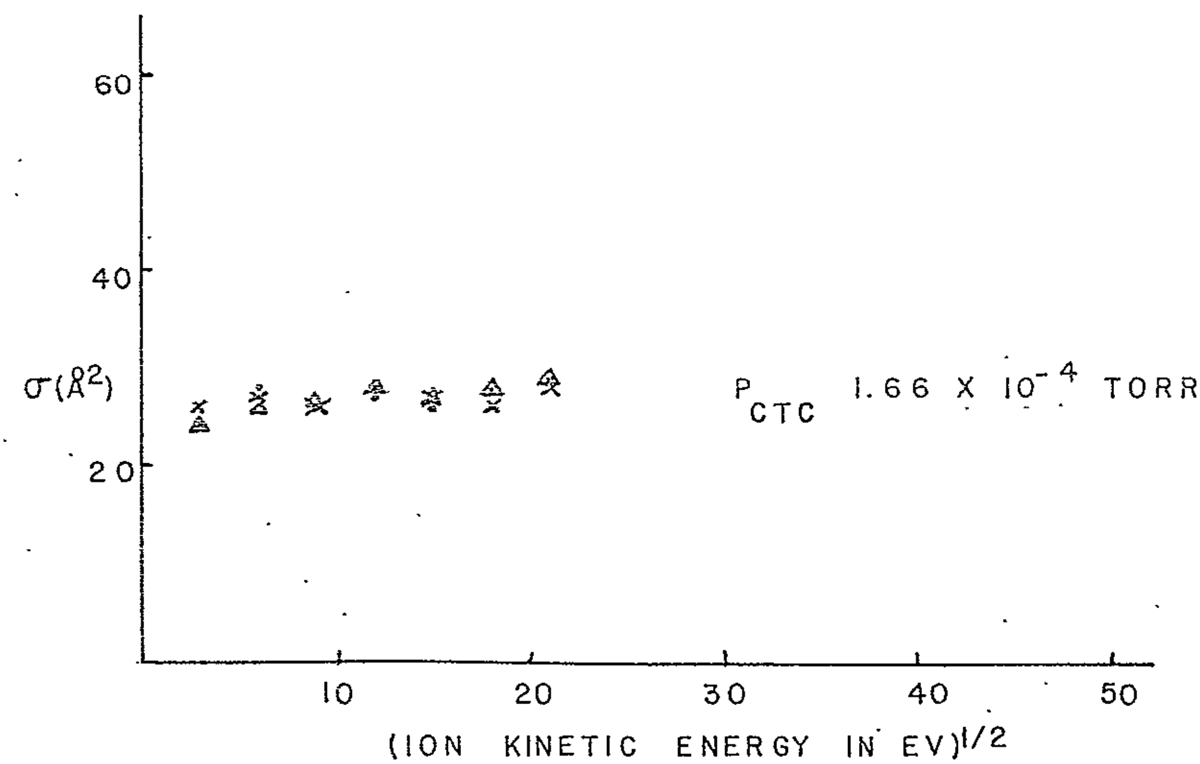
60
40
20
σ(Å²)
10
20
30
40
50
(ION KINETIC ENERGY IN EV)^1/2
P CTC 1.66 X 10^-4 TORR

Fig. 6

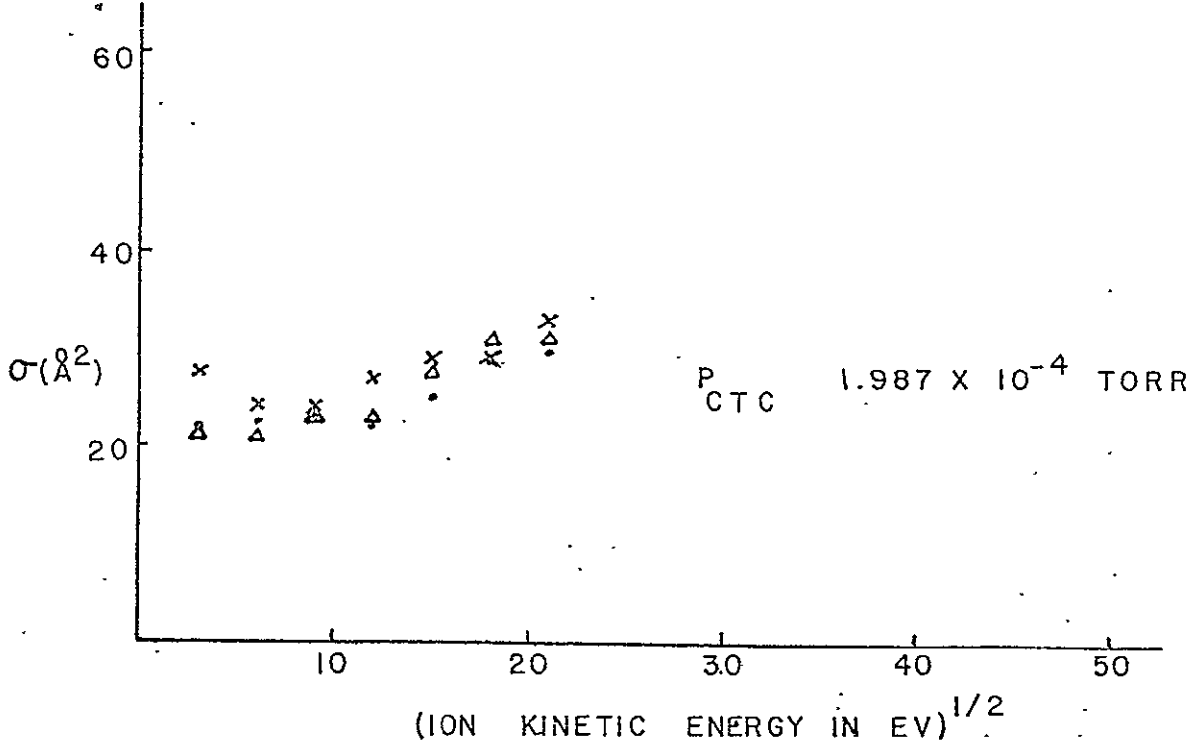
60
40
20
σ(Å²)
P_{CTC} 1.987 X 10⁻⁴ TORR
10
20
30
40
50
(ION KINETIC ENERGY IN EV)^1/2

Fig. 7

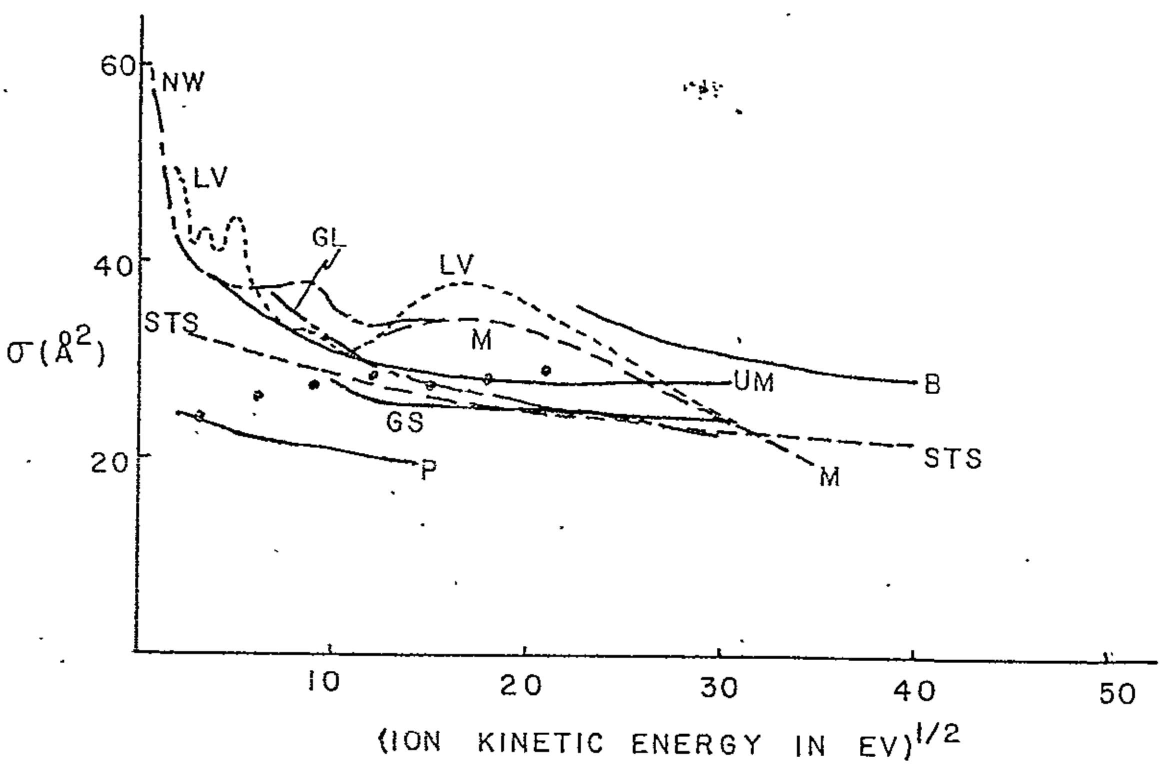
60
40
20
σ(Å²)
NW
LV
GL
LV
M
STS
UM
B
GS
P
STS
M
10
20
30
40
50
(ION KINETIC ENERGY IN EV)^1/2

Fig. 8

COLLISION TIMES

Electronic, vibrational, and rotational transitions will be important only when such transitions can take place during the time of the collision. The vibrational and rotational periods of N_2 are $\tau_{vib} \sim 2 \times 10^{-14}$ sec and $\tau_{rot} \sim 2 \times 10^{-12}$ sec.[1] The collision time, i.e., the lifetime of the ion-molecule complex, is $\tau_{coll} \sim 2.4(R/v)10^{-17}$ sec in atomic units.[1] The range of incident energies, 9 eV $< E <$ 441 eV, or speeds $5 \times 10^{-3} < v < 4 \times 10^{-2}$ (in atomic units), is the same order of magnitude as the speed range of $7 \times 10^{-3} < v < 6 \times 10^{-2}$ given by Flannery et al.[1] These speeds involve large interaction radii $10 > R > 5$, for the collision. Then the collision times are in the range 4.7×10^{-14} sec $> \tau_{coll} > 3.4 \times 10^{-15}$ sec. Therefore the collision times are much much less than the time of rotation, and the collision is finished before the ion-molecule complex can rotate. However, the collision time is the same order of magnitude as the vibrational time, and a vibrational transition is highly likely during the collision.

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DECAY OF EXCITED STATES OF N_2^+

For the measurement of total charge-transfer cross sections, consideration should be given to the lifetimes for the existence of the various excited states of N_2^+. The length of the Langley charge transfer cell (CTC) is 1.985 inches, or 5.0419 cm. For an ion of incident energy 9 eV, or incident speed 7.87×10^5 cm/sec, the time spent in the CTC is on the order of 6.41 μsec; for an ion of incident energy 441 eV, incident speed 5.51×10^6 cm/sec, the time is of order 0.915 μsec. Since the electron energies to produce the N_2^+ were selected to be between 16 and 20 eV in the Langley experiment, only the ground state $N_2^+(X^2\Sigma_g^+)$ and the first two excited states, $N_2^+(A^2\Pi_u)$ and $N_2^+(B^2\Sigma_u^+)$ need to be considered. The lifetimes of the $B \rightarrow X$ radiative transitions are on the order of 60 nsec,[1,2] so that all the $N_2^+(B^2\Sigma_u^+)$ ions formed in the electron impact ionization undergo transitions to the ground state $N_2^+(X^2\Sigma_g^+)$ within the source region. The lifetimes of the $A \rightarrow X$ radiative transitions are on the order of 10 μsec.[3,4,5] These ions undergo transitions which occur exponentially with distance as $e^{-t/\tau}$ where τ is given in the following table for the first few vibrational levels.[3] The presence of some undecayed $N_2^+(A^2\Pi_u)$ states was included by Flannery et al[6]

since the ions were contained for 9.6 - 14.2 μsec in their time-of-flight apparatus.

The percent of (electronic and vibrational) ground state $N_2^+(X^2\Sigma_g^+, v'=0)$ in the reactant ion beam as a function of ionizing electron energy from 0 to 100 eV is presented in Fig. 4 of Ref. 6. For energies of 16, 17.5, and 19.5 eV (those used at Langley), it can be deduced from this figure that between 80 and 90 percent of the incident ion beam must be in the ground state $N_2^+(X^2\Sigma_g^+, v'=0)$.

v'	τ (μsec)
0	15.5
1	13.7
2	12.2
3	11.0
4	9.9
5	9.1
6	8.4

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